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Effect of Phosphorus Content in Nickel Phosphide Catalysts Studied by XAFS and Other Techniques

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Introduction: Transition metal phosphides are a new class of high-activity hydroprocessing catalysts, among which nickel phosphide is the most active. A series of novel, supported nickel phosphide catalysts (Ni_2P/SiO_2) were synthesized by means of temperature-programmed reduction (TPR), and the effect of phosphorus content on hydroprocessing performance and catalyst structure were studied.

Methods and Materials: The preparation of the supported phosphides was carried out in two stages. First, a solution of the metal and phosphorus components was impregnated on the carrier silica support and the material was dried and calcined to form supported phosphates. Second, the phosphates were transformed into phosphides by temperature programmed reduction (TPR). The catalysts were characterized by BET surface area determinations, CO uptake titrations, x-ray diffraction (XRD) analysis, elemental analysis, and extended x-ray absorption fine structure (EXAFS) measurements. The activity of the catalysts was studied in a three-phase trickle bed reactor operated at 3.1 M Pa and 643 K in the hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) of a model liquid feed containing 2000 ppm nitrogen as quinoline, 3000 ppm sulfur as dibenzothiophene, 500 ppm oxygen as benzofuran, 20 wt % aromatics as tetralin, and balance aliphatics as tetradecane. References for the EXAFS studies were prepared by ampoule techniques, involving heating the elements in evacuated quartz cells at 1273 K.

Results: The samples were prepared with initial Ni/P ratios of 2/1, 1/1, 1/1.8, 1/2, 1/2.2, and 1/3, but the samples with excess P lost some of their P content during reduction and the main phase obtained was Ni_2P. The activity and stability of the catalysts were affected profoundly by the phosphorus content, both reaching a maximum with an initial Ni/P ratio of about 1/2 (actual Ni/P = 1/0.57 after reaction). At this optimal P content, the activity was excellent, with steady state HDS conversion of 100 % and HDN conversion of 81 %, which were much higher than that of a commercial Ni-Mo-S/Al_2O_3 catalyst with corresponding HDN conversion of 76 % and HDN conversion of 38 %. The stability of the optimal composition was also high, with no deactivation observed over 90 h in HDS and only a slight deactivation in HDN. EXAFS analysis of the catalysts indicated the formation of a Ni_2P phase for the sample with an initial Ni/P ratio of 1/2 which was retained after reaction. At lower P content some Ni metal and $Ni_{12}P_5$ was obtained, and at higher P content, the Ni_2P active phase was blocked by excess P.

The EXAFS spectra of the fresh and spent samples with initial Ni/P ratios of 2/1, 1/2, and 1/3 showed that changes occurred in the catalysts after reaction. For the spent sample with initial Ni/P = 2/1, a small feature appears in between the main Ni-Ni peak and the Ni-P shoulder. For the spent sample with initial Ni/P = 1/2, a two-peak structure is retained, but there is a reduction in the Ni-Ni peak intensity. For the spent sample with initial Ni/P = 1/3, the Ni-Ni peak is almost entirely attenuated and a broad feature at lower interatomic distance appears. Clearly, in all cases there is disruption of the original Ni_2P phase, and this is likely due to the formation of sulfur compounds. Nickel carbide and nickel nitride are unstable at the conditions of reaction. The identification of the changes occurring in the spent samples was carried out by comparing their spectra to those of bulk sulfide references (Fig. 1).

Conclusions: The activity results and characterization by EXAFS indicate that on these novel catalysts, the HDN reactions are structure-sensitive while the HDS reactions are structure-insensitive.

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References: S. T. Oyama, X. Wang, Y.-K. Lee, K. Bando, F. G. Requejo, “Effect of Phosphorus Content in Nickel Phosphide Catalysts Studied by XAFS and Other Techniques”, J. Catal. **210** (2002) 207.

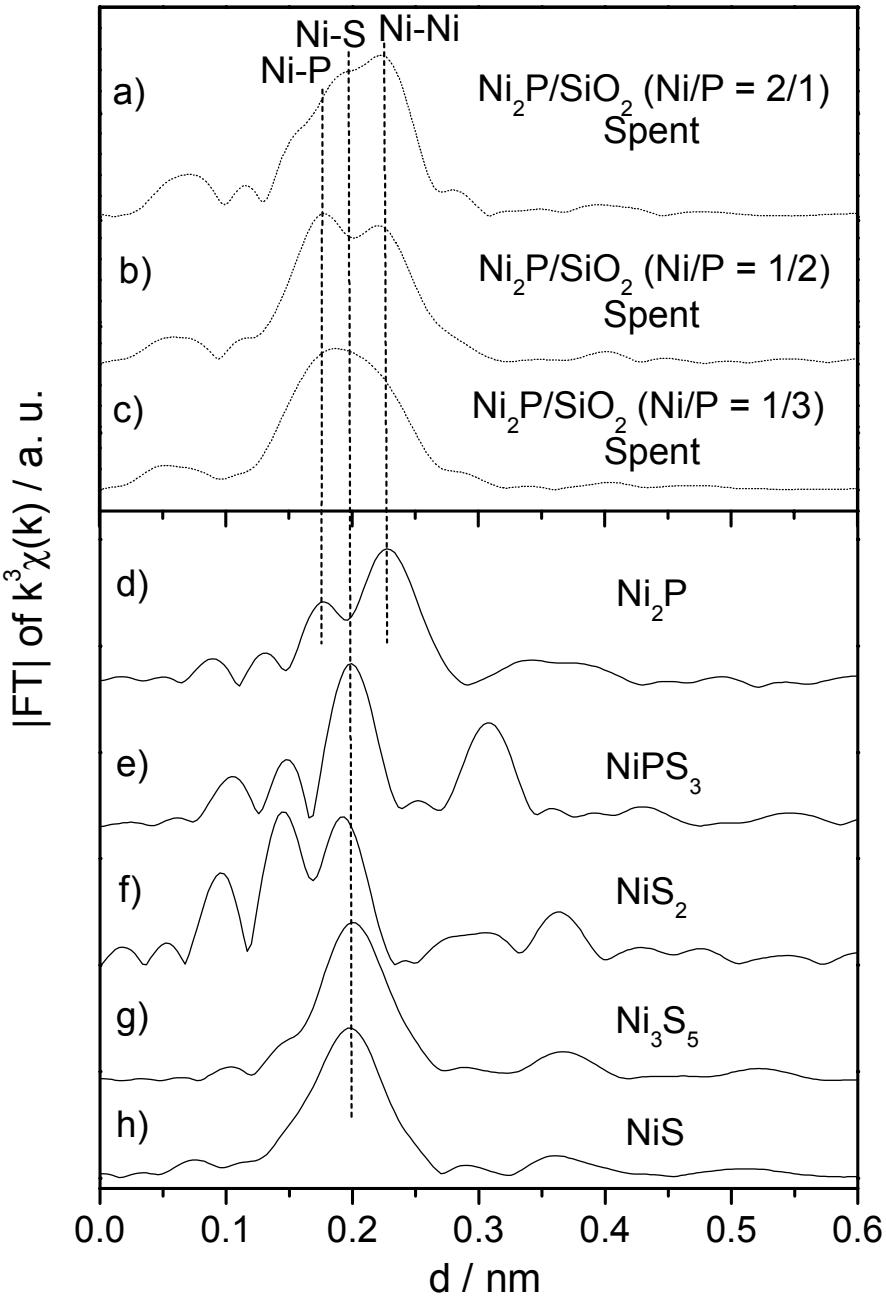

Figure 1. Comparison of Nickel K-edge EXAFS for the spent samples with Ni/P ratios of a) 2/1, b) 1/2, c) 1/3 and references d) Ni_2P, e) $NiPS_3$, f) NiS_2, g) Ni_3S_5, h) NiS. The Ni/P ratios indicated are initial values.